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EXPLORATORY DEVELOPMENT OF CONDUCTIVE COATING MATERIALS 1/1

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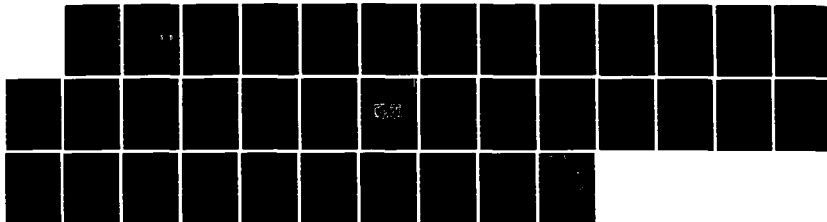
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Part II

EXPLORATORY DEVELOPMENT OF CONDUCTIVE COATING MATERIALS

*SRI INTERNATIONAL
333 RAVENSWOOD AVENUE
MENLO PARK, CALIFORNIA 94025*

DECEMBER 1978

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Final Report for Period 24 June 1977 to 24 October 1978

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AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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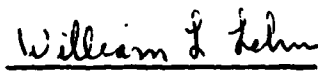
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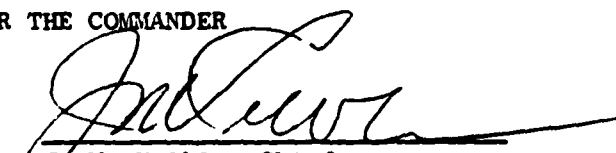
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William L. Lehn
Project Engineer

FOR THE COMMANDER


J. M. Kelble, Chief
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FOREWORD

This report was prepared by SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025, under Contract No. F33615-77-C-5080. It was initiated under Program Element 62102F, Project 2422, "Protective Coatings and Materials," Task No. 242201, "Protective Coatings and Materials," Work Unit No. 24220105. This work was administered under the direction of the Coatings and Thermal Protection Materials Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Mr. Michael J. Moscyński and Dr. W. L. Lehn, AFML/MBE, served as project engineers. Dr. S. Roy Morrison was the project leader. Others who contributed to the research were M. Landstrass, D. Parkinson, and K. Frese, Jr.

This report covers work for the period 24 June 1977 to 24 October 1978.

CONTENTS

LIST OF ILLUSTRATIONS	v
LIST OF TABLES	v
I SUMMARY	1
II TECHNICAL DISCUSSIONS	5
A. Pigment Preparation	5
B. Flocculation	10
1. Flocculation at a Wire	11
2. Flocculation at a Rod	11
C. Coupling Agent Addition	16
1. Floc Strength	16
2. Pigment/Coupling Agent Interaction	17
D. Dispersion of Chain Floccs in a Vehicle	20
1. Dispersion in a Solvent	20
2. Introduction of the Dispersed Floccs into a Vehicle	20
E. Resistance of Chain Flocculated Pigments	21
1. Resistance Versus PVC in Air	21
2. Preparation and Testing of Optimized Coating	25
F. Samples Submitted to WPAFB	27
III RECOMMENDATIONS	28



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LIST OF ILLUSTRATIONS

1.	Chain Floccs Produced in a High Frequency Field	13
2.	Reactor for Chain Floc Growth	14
3.	Resistance of Chain-Flocculated SnO ₂ as a Function of PVC	22

LIST OF TABLES

1.	Extinction Coefficient ϵ (cm ² /g) as a Function of Wavelength in ZnO:Ga and SnO ₂ :Sb (1 At% Additive) . .	7
2.	Average Particle Size for ZnO:Ga and SnO ₂ :Sb as a Function of Additive Concentration	9

I SUMMARY

The overall goal of the program was to develop antistatic coatings for use on aircraft radomes. The required properties are:

- High flash resistance;
- High erosion resistance; and
- Moderate surface conductance, ————— See

Because of these three requirements, a specific form of the pigment/vehicle combination will be needed. Because a light color is mandatory for satisfactory flash resistance, a conductive white pigment must be developed. If a conductive white pigment is available, other colors can be easily prepared, whereas the reverse is not true. For satisfactory erosion and weathering resistance, the pigment volume concentration (PVC) must be kept low, and therefore a pigment of high hiding power must be used. For satisfactory conductance, the contact resistance between pigment particles and between flocs must be low and reproducible. For low interfloc conductance (with low PVC), the pigment particles must flocculate to form chains, rather than compact clusters. Cluster formation at low PVC will lead to poor conductance because the large distances between clusters are filled with insulating polymer. With chain flocculation, however, moderate contact between chains provides the needed conducting paths while permitting low PVC for erosion resistance. In essence, we are comparing flocs in a "hailstone" form with flocs in a "snowflake" form. In both cases interfloc contact is required for conductance, but with the "snowflake" form (chain flocculation), the PVC will be much lower and erosion resistance much greater.

The problems are as follows:

- (1) Flocculation--A white pigment material must be prepared so that, in an organic binder (polyurethane or fluorocarbon), chain flocs of pigment will result from solvent evaporation. This has been the dominant problem addressed in the work conducted at SRI.
- (2) Conductivity--The white pigment material must have a reasonable bulk conductance; more important, the intergranular and interfloc contact resistances must be kept low and reproducible. Intergranular conductance can be attained by heavy doping,¹ but substantial work is needed to improve the reproducibility, the color, and probably the long-term stability of the coating in air.
- (3) Hiding power and color--Because a white pigment will satisfy all the color requirements, developing a white pigment was clearly the objective. A pigment of good hiding power is desirable. Obviously, the preferred pigment was rutile (at a particle size of 0.25 μm) because of its extremely high index of refraction. Other pigment materials to be examined should compare as favorably as possible with this ideal.
- (4) Binder--The choice of binder is restricted by erosion resistance and stability requirements. In particular, the treated pigments must be compatible with polyurethane or fluorocarbon vehicles.²

In this program we have emphasized the study of flocculation. We developed a technique based on electric field-induced flocculation, followed by "cementing" the chains into a permanent structure using a

¹General Electric Company, "Electrically Conductive Coating Materials," AFML-TR-73-207 (October 1974).

²A. I. Medalia and F. A. Heckman, Carbon 7, 567 (1969).

SiCl_4 coupling agent. Once the techniques of chain flocculation had been optimized, several other steps were necessary before a satisfactory coating could be developed, namely:

- (1) Produce enough chain flocs to make bulk tests of their stability and conductive properties, and modify production and doping techniques to meet the requirements.
- (2) Select the best pigment-- TiO_2 , ZnO , or SnO_2 --on the basis of the most satisfactory results in (1).
- (3) Develop methods for incorporating chain flocs into binders to form a conductive paint.
- (4) Study means of producing the optimal paint, simultaneously evaluating conductance, flow, whiteness (flash resistance), and erosion resistance.

The accomplishments can be summarized in terms of the development of (a) techniques for chain formation, (b) techniques for chain "cementing" to form good intergranular conductance, and (c) testing.

Production of gram size quantities of chain flocculated pigment was accomplished through a redesigned reactor. This reactor employed a large area electrode and operated with audio frequency (10-20 KHz). High voltage fields enabling growth of $\sim .5$ gm of chain flocculated pigment per day.

Chains of TiO_2 , ZnO , and SnO_2 , cemented by a $\text{SiCl}_4:\text{H}_2\text{O}$ reaction, were grown successfully in this reactor. However, the ZnO chains were covered by a water-soluble ZnCl_2 film; and ZnO was therefore unacceptable as a pigment. When the SnO_2 and TiO_2 chain flocs with SiO_2 cementing films were treated at high temperature they were strong enough to be dispersed in a vehicle. However both SnO_2 and TiO_2 chains prepared by this technique were found to be semi-insulating. The high resistance was traced to an excessively thick SiO_2 layer in the intergranular contacts. Attempts to correct this problem included a subsequent gas phase HF

treatment. This treatment made the chains conductive but was found to weaken them. Satisfactory conductive chains were grown by the addition of a SnO_2 phase on top of the SiO_2 phase used to cement the pigments particles together. This was achieved by the addition of SnCl_4 and H_2O to the reactor after the chains had been cemented using the $\text{SiCl}_4:\text{H}_2\text{O}$ reaction. Both SnO_2 and TiO_2 chains were prepared by this method. These chains were incorporated into both fluorocarbon and polyurethane vehicles to produce conductive coatings.

The bulk resistivity of paint formed with these pigments was as low as 10^{-2} cm using a 35% PVC. The resistivity could be increased at will by pre-firing the pigment. A bulk resistivity of about 1000^{-2} cm is needed to produce paint that has the required 10^6 ohms/square when it is applied at reasonable thickness; thus, the objective of the program--developing a pigment of the correct resistivity at low PVC (for erosion resistance)--was met.

However, further work is needed to improve the whiteness of the pigment and to test the long-term stability of the conductance. Although the pigment is formed from white TiO_2 , SiO_2 , and SnO_2 , and therefore should be white, the resulting material is noticeably gray. The problem should be solvable but lack of time prevented a thorough investigation. Similarly, long-term stability could not be studied because a satisfactory pigment was produced late in the study period.

II TECHNICAL DISCUSSIONS

A. Pigment Preparation

As was indicated in the Introduction, three pigments were studied: TiO_2 , ZnO , and SnO_2 .

We developed a satisfactory method for preparing conductive TiO_2 . For each kilogram of TiO_2 used, 0.13 mole NbCl_5 is dissolved in 750 cc of 14 M HCl , and the solution is diluted with 2.25 liters H_2O . This solution is mixed with Baker reagent grade TiO_2 (anatase).

The mixture is stirred 15 minutes, then neutralized with 4 M NH_4OH to pH 7 to precipitate the niobium additive. The pigment is washed twice by centrifuging, and then dried, first at 100°C , then at 400°C . It is calcined at 1180°C for 18 hours to diffuse the Nb and convert the TiO_2 to rutile and then cooled rapidly.

The resulting cake is ball milled in cyclohexane (with the dispersing agent AOT added) for several days, followed by two washes in cyclohexane to remove excess AOT. A soak for 18 hours in 50 M $\text{HF}/18\text{ M } \text{HNO}_3$ to remove excess Nb_2O_5 is followed by a water wash, and an NH_4OH wash at pH 12 or 13 is used to remove adsorbed fluoride. A wash in water is followed by a 160°C treatment to remove NH_3 and residual fluorides. The resulting agglomerated material is broken up and screened.

The resulting pigment is light gray-blue because of the unavoidable absorption band of the free electrons added to the TiO_2 . The use of compensating impurities will not improve the color of the pigment. Using lower Nb concentrations, however, produces a whiter pigment. The electron density needed to reach the desired conductance was not determined, so the final extinction coefficient for this pigment cannot be predicted.

Studies were also made of the doping of ZnO with Ga and of SnO₂ with Sb. The ZnO samples were prepared by co-precipitation. Specifically Zn(NO₃)₂·6 H₂O and Ga(NO₃)₃·9 H₂O in the weight ratio 180:1 were dissolved in water, then NH₄OH was added to cause co-precipitation at pH ~ 9. After filtering and drying (150°C) the sample was heated to 100°C for 1 hr to promote diffusion. The SnO₂:Sb samples were prepared by mixing highly dispersed powders in the appropriate ratio and calcining at 800-1000°C to promote interdiffusion.

For ZnO:Ga, higher calcining temperatures (to 1100°C) favor higher free electron density, as measured by infrared absorption. In these measurements the ZnO:Ga powders are dispersed in a KBr matrix and the optical absorption versus wavelength determined. As free electron absorption occurs in a wavelength region between about 3 μm and 7 μm, qualitative comparison of the free electron densities for various samples is straightforward. A lower calcining temperature (about 875°C) gives the highest electron density for SnO₂:Sb. Comparison of extinction coefficients (ε) as a function of wavelength (in μm) for the two systems (Table 1) suggests that at lower wavelengths (< 7 μm), higher values for ε are observed for SnO₂:Sb. Above 7 μm, ε values for ZnO:Ga are larger.

When we were ready to undertake tests of ZnO coatings we had identified a commercial source for conductive (Al-doped) ZnO pigment and used that in the tests rather than attempting to prepare our own by the above recipes. The commercial source is the St. Joe Mineral Corporation who market the conductive ZnO under the designation BS-F-1.

For use in preparing coatings, the SnO₂ pigment was prepared as follows. Baker SnO₂ was slurried in acetone (2 ml/g) with SbCl₃ dissolved in the acetone to provide 0.5 wt% Sb in the SnO₂. The acetone was evaporated and the pigment calcined at 800°C for 1.5 hours to induce

Table 1

EXTINCTION COEFFICIENT ϵ (cm^2/g)
 AS A FUNCTION OF WAVELENGTH
 IN ZnO:Ga AND SnO₂:Sb
 (1 At% Additive)

Wavelength (μm)	ZnO:Ga (1100°C/1 hr)*	SnO ₂ :Sb (800°C/1 hr)*
3	100	1450
4	280	1580
5	450	1300
6	620	1040
7	780	850
8	900	750
9	1000	710
10	1060	700

* Calcination conditions

Sb diffusion into the SnO_2 , followed by a fast cool. The resulting pigment is off-white but highly conducting.

As shown in Table 2, the average particle size for both systems, as determined from N_2 chemisorption at 77°K, appears to vary with the concentration of the additive. The size of the SnO_2 :Sb crystallites is much smaller than that of SnO :Ga, but a general decrease in size was observed for both systems as the additive concentration increased.

The color of the ZnO :Ga system remains nearly white over the additive concentration range studied (about 1.2 to 2.0 at%), but the SnO_2 :Sb system is blue-gray with heavy Sb doping. Studies of compensating impurities in SnO_2 :Sb were initiated to attempt to minimize the blue-gray coloration. Since Sb^{+5} is calculated to have a substantially lower ionic radius than Sn^{+4} , we attempted to use larger ions for compensation. Addition of Pb, Bi, or Zr showed no substantial improvement in preliminary studies.

We made preliminary measurements of the interparticle conductivity as influenced by surface additives, using TiO_2 (doped with 1% Nb) as the conducting pigment. In these measurements the pigment is pressed into a pellet and four-point conductance measurements are made. The samples are outgassed at 400°C to remove oxygen. The conductance depends on interparticle contacts, and so depends strongly on any surface additives.^{2b} Thus the effect on interparticle conductance of surface additive is determined by impregnating the powder with the additive of interest before pressing the pellet. Adding cerium (IV) additive provides a surface state 0.6 eV below the TiO_2 "conduction band" and decreases the

^{2b} S. R. Morrison, Surface Sci. 27, 586 (1971).

Table 2

AVERAGE PARTICLE SIZE FOR ZnO:Ga AND SnO₂:Sb
AS A FUNCTION OF ADDITIVE CONCENTRATION

Additive Concentration (at%)	Size (Å)	
	ZnO:Ga (1100°/1 hr)*	SnO ₂ :Sb (800°/1 Hr)*
0	159,000	833
0.2	31,000	770
0.5	11,000	680
1.0	4,000	550
2.0	23,000	392

* Calcination conditions

conductance at room temperature by about four orders of magnitude. We used this additive in our preliminary tests to simulate the way in which oxygen lowers the conductance, because effects of oxygen are harder to standardize. We studied an aquo Fe(III) additive that has an energy level 0.4 eV below the TiO_2 "conduction band," and we have studied additives with Zn(II) and Cr(III). None has shown a substantial effect on the conductance. However, with $\text{K}_3\text{Fe}(\text{CN})_6$ as a surface additive, the conductance of a pressed TiO_2 pellet is two orders of magnitude higher than with no additive. Both the treated sample and the blank were vacuum-treated to remove adsorbed oxygen. On the simplest theoretical basis under such conditions the blank sample should show a conductance equal to or greater than that with any additive oxidizing agent. A possible reason for the extra conductance associated with the ferri-cyanide may be the addition of levels at the polaron level in the TiO_2 that would permit polarons to undergo surface-state tunneling.

B. Flocculation

As was described in the Summary, the dominant problem in this program was to induce white oxide pigments to flocculate in the form of chains, thereby permitting a conductance mechanism like that in conducting carbon paints. The approach was based on the Winslow effect³ in which an electric field induces chain flocculation by causing dipole formation in each particle. Such effects are common and are usually of interest because of their importance in viscosity⁴ and are thus termed electroviscous effects. Because an ac potential is used, the dielectrophoretic effect provides the force rather than an electrostatic

³W. M. Winslow, J. Appl. Phys. **20**, 1137 (1949).

⁴D. L. Klass and T. W. Martinek, J. Appl. Phys. **38**, 75 (1967).

or electrophoretic effect.

1. Flocculation at a Wire

Our early studies of flocculation involved chain floc production on a 0.003 inch platinum or nichrome wire. Because the yield of flocs per pass was low, it was necessary to automate the apparatus and alternate floc growth with floc removal from the wire (by scraping). Although later in the program it was found (see below) that the chain flocculation could be induced much more rapidly with a rod and a high frequency field, the period spent attempting to automate the wire-based apparatus was of value. Studies of the temperature dependence of the growth rate and of the effects of temperature programming on floc strength made during this period were valuable in later work. Chain growth on a wire was easier to achieve (presumably because of the higher electric fields), but it was much slower, and therefore much less attractive than chain growth on a rod. Because the wire technique was not brought to a successful process before it was abandoned in favor of the rod technique, we will not describe the studies connected with growth at a wire in this report.

2. Flocculation at a Rod

Part way through the program, a significant improvement was made that permitted the formation of chain flocs on a rod (about 3/8 inch in diameter), the large surface area of which permitted a larger yield per pass. In all our earlier studies, we used 60 Hz ac voltage to provide the field for dielectrophoretic attraction of the particles to the high field electrode. We discovered accidentally that, unless conditions are well controlled, the 60-Hz ac voltage applied to a wire actually repelled many of the smallest pigment particles. We theorized that if a small pigment particle becomes charged, it will oscillate in the 60-Hz field and gain sufficient kinetic energy to scatter other

small particles. To avoid that problem, we increased our operating frequency of 10 to 20 kHz. The results were a vast improvement in the rate of chain growth on wires, improvement in the shape of the chain flocs, and the ability to use a large area center electrode to replace the wire electrode.

Figure 1 is a photograph of typical chains resulting from this improved technique. In this case the chains were grown at 15 kHz on a wire, but the results are similar using the thicker rod. The microscope's limited depth of focus makes some sections of the flocs look blurred.

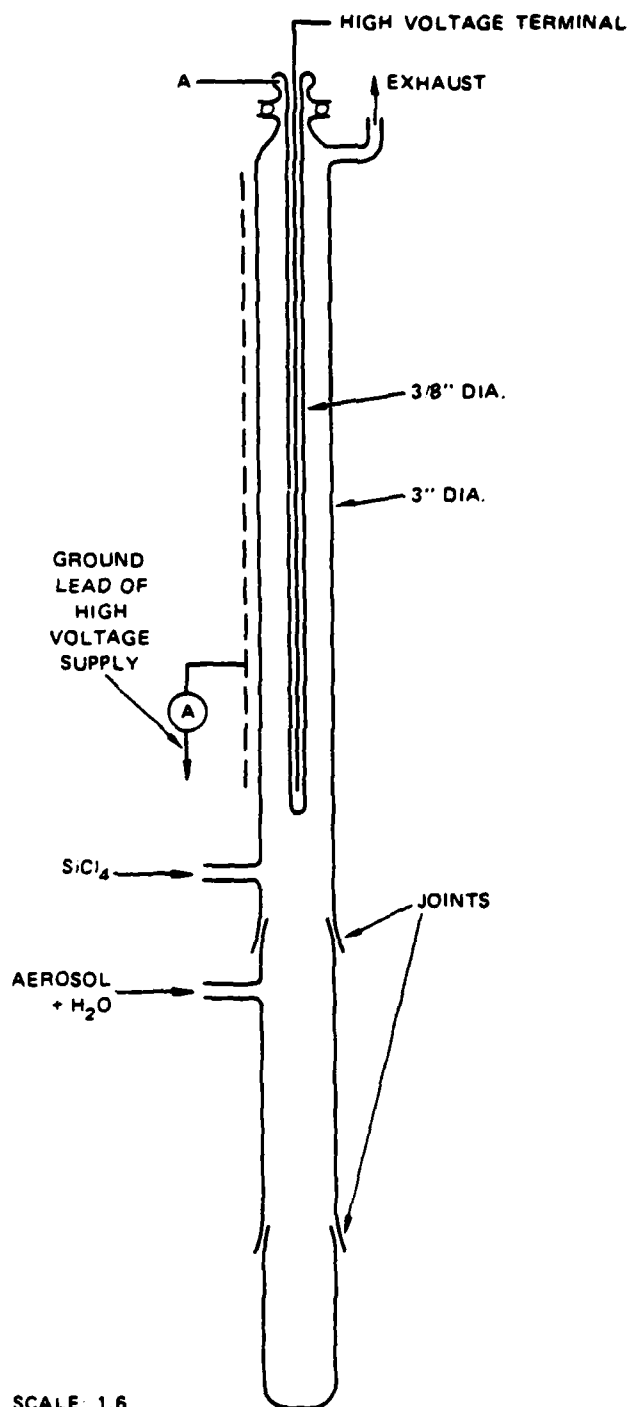
Figure 2 is a diagram of the apparatus used for flocculation on a glass rod. It consists of a glass cylinder about 3 inches in diameter in which the inner glass tube is centered. A metal rod is inserted into the inner tube for the high voltage lead. On the outside of the reaction chamber, shown as a dashed line, is the low voltage terminal, connected through an ammeter to the ground of the high voltage supply. The diameter of the inside tube is the order of one quarter to three-quarters of an inch. The aerosol is introduced through the bottom entry and passes slowly up through the reaction chamber; excess aerosol and gas exit near the top of the apparatus. At the very top of the apparatus is a dead space, marked A, which is partially blocked from the main reactive chamber in an attempt to prevent pigment particles from reaching the dead space. The object here is to prevent the pigment particles from forming a continuous conducting path between the outside of the inner tube and the inside of the outer wall. The point is, of course, that even with a very small leakage path to short the glass walls, it is found that the aerosol no longer is in a region of high electric field.

The major difference between this design and the earlier "wire" design is the large radius high voltage electrode. The large radius



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FIGURE 1 CHAIN FLOCS PRODUCED IN A HIGH FREQUENCY FIELD



SCALE: 1.6

SA-6492-4

FIGURE 2 REACTOR FOR CHAIN FLOC GROWTH

leads to a much higher area for floc growth, but much lower electric fields.

The ac ammeter, shown connected between the ground terminal of the reaction chamber and the ground terminal of the high voltage apparatus, is used to detect any electric breakdown in the reaction chamber. These breakdowns occur at the high frequency employed in spite of the glass insulation between the metal electrodes and the reaction chamber. The glass surfaces of the reaction chamber become coated with conducting pigment particles. The capacitative impedance across the glass is low, so that these conductive coatings become respectively the high and low voltage electrodes. Therefore, a very high voltage appears across the aerosol. If electrical breakdown occurs and a plasma develops, chains no longer form. The reason that plasma formation prevents chain formation may be that the particles acquire a high electrostatic charge or that the electric field gradient becomes too weak. In any case, it is clear that plasma effectively prevents chain formation. If the ammeter is in the circuit, we can easily check the linearity of the current/voltage characteristics and observe the voltage at which breakdown begins. Some of the troubles in growing chain flocs before this precaution was taken are now traceable to an excessive voltage applied to the apparatus.

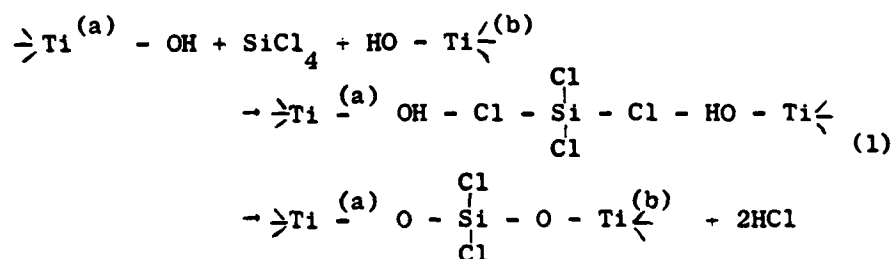
The simple apparatus shown, without further modification provides about 0.1 g of chain flocs in a run of about 2 hours. Typically, the applied voltage is 1500 to 2000 V, aerosol flows at 3 liters/min with 8 torr H_2O and 0.1 torr $SiCl_4$ in the flow. The pigment settles as chains on the center tube. The chlorosilane and water interact as described in the next section to cement the growing chains. We find that chains can grow several millimeters and up to a centimeter in length if desired.

C. Coupling Agent Addition

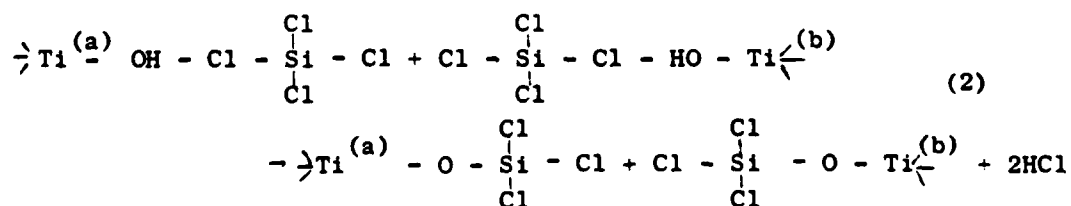
1. Floc Strength

In our earlier studies we found that SiCl_4 deposited on oxide pellets provided a substantial bond between particles. However, early in the present work we determined that the strength of TiO_2 chain flocs prepared and "cemented" simultaneously by adding SiCl_4 to the aerosol was inadequate. When the chain flocs were placed in a solvent with a dispersing agent strong enough to disperse the pigment, the chain flocs disintegrated.

We concluded that because the SiCl_4 and the TiO_2 particles were mixed before entering the reaction chamber and thus entered it simultaneously, the SiCl_4 adsorbed as a monolayer on the TiO_2 before forming chains in the apparatus. Instead of causing the desired reaction, in which SiCl_4 attacks OH groups at the TiO_2 surface:



we have the silane adsorbed while the TiO_2 is still in the aerosol and the reaction becomes:



where $Ti^{(a)}$ and $Ti^{(b)}$ represent titanium atoms on adjacent particles of TiO_2 . In Reaction 1, the titanium atoms become linked through the Si - O bonds, but in Reaction 2 when the surface is entirely covered with $SiCl_4$, no such favorable bond can form.

Several methods for correcting this problem were tested. All involved using water vapor alternately or simultaneously with the $SiCl_4$, and several of them were successful.

The simplest procedure, which was adopted in the end with $SiCl_4$, was to use a mixture of H_2O and $SiCl_4$ in the ratio 80/1, and keep the flocs at room temperature. Subsequently heating the flocs to $T > 500^\circ C$, either in the reaction chamber or in a separate furnace, produces strong flocs, presumably by completing the formation of Si-O linkages.

2. Pigment/Coupling Agent Interaction

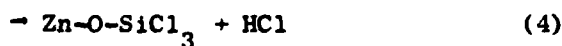
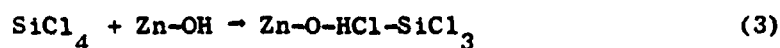
Three pigments, TiO_2 , ZnO , and SnO_2 were tested for use in chain flocs. The TiO_2 pigment was by far the easiest to handle because it has a high dielectric constant and therefore easily forms the chains in a minimal electric field, and because it is quite unreactive, compared to ZnO and SnO_2 .

The pigment zinc oxide has the advantage of being readily available commercially in a conductive form. Thus, it was the second pigment used for chain floc preparation. The ZnO used was from the St. Joe Mineral Corporation, stock number BS-F-1.

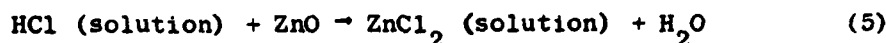
It became apparent early, however, that the ZnO pigment has problems during chain formation that were not observed with the TiO_2 pigment. For example, although the ZnO pigments formed what appeared to be satisfactory chains when observed in the apparatus, when scraped from the collection tube they agglomerated, losing their chain-like

structure. Also, it was found that the application of trimethylchlorosilane (TMCS), which was used for improved dispersion of the TiO_2 pigment, caused further trouble with ZnO_2 pigment--in fact, the pigment dissolved in the TMCS.

From these and similar observations we concluded that the problem was associated with the solubility of ZnO in hydrated HCl. Apparently, the SiCl_4 reacts with the hydroxylated surface of the ZnO as follows:



but in a moist environment, the HCl dissolves the ZnO:



and regenerates hydroxyl groups. Thus reactions, (3) through (5) can continue until all the available SiCl_4 is consumed in forming ZnCl_2 . Since ZnCl_2 is hygroscopic, an intermediate ZnCl_2 layer weakens the chains, the presence of ZnCl_2 would probably reduce the intergranular conductance, although we did not test this property.

It was considered possible that the problem with ZnO could be overcome by careful control of the temperature and time of the silane and water introduction. In other words, it may well be possible to adjust the temperature so that the HCl produced in the reaction desorbs rather than solvates on the moist ZnO surface. However, correcting this problem seemed much more difficult than switching to the SnO_2 pigment.

The formation of chains using the SnO_2 pigment showed some of the characteristics observed earlier with ZnO pigment but in a much more

moderate form. Whereas the ZnO pigment when removed from the apparatus tended to form a massive ball of gel-like appearance, in our initial studies the removed SnO_2 pigment showed clear chain formation. The chains were extremely sticky, however, and clung together in what could be considered bundles of chain flocs.

Two approaches to resolve this problem were tested: (1) one was to form the chains at a high temperature; and (2), to form the chains with minimal amounts of SiCl_4 added to the gas stream. We first tested the high temperature preparation. It was found experimentally that HCl desorbs from the SiCl_4 -treated SnO_2 at a temperature of about 200°C . Thus we grew chains at 200°C to keep the HCl concentration low and to prevent reactions analogous to equation (5). This approach was found unsatisfactory because the chains formed had very little strength. They were difficult to remove from the apparatus because they collapsed immediately when the electric field was removed. Presumably, the adsorption of SiCl_4 on the hydroxylated SnO_2 surface was too low at 200°C .

Chains formed using the second method, using a low concentration of SiCl_4 at room temperature, retained their sticky quality. However, by adjusting the SiCl_4 pressure, we were able to obtain a satisfactory compromise between chains weakness and chain stickiness. It was found experimentally that rather than scraping the chains off, a slight tapping of the apparatus was enough to cause the chains to fall off, and under these conditions the chains did not agglomerate. With the chains removed in this way, a subsequent treatment, a 500°C anneal in air, caused the chains to lose their stickiness. Presumably this high temperature treatment drives off H_2O and HCl and completes the conversion of the coupling agent to the siloxane form. Chains formed in this way are found strong enough to withstand ultrasonic dispersion in MEK

(our standard test to show that the chains are strong enough to be introduced into a vehicle).

D. Dispersion of Chain Floccs in a Vehicle

1. Dispersion in a Solvent

No apparent difficulties were encountered regarding the dispersion of chain floccs in a solvent. Dispersion in MEK is fairly complete, as inferred from very long settling times. We have also observed complete dispersion in trimethylchlorosilane and in a solution of trimethylchlorosilane and acetone. The pigment flocculates in water. The rate and degree of dispersion were increased by an ultrasonic treatment in the solvent, using a Bransonic 220 ultrasonic unit. Such improvement in dispersion could be expected.

2. Introduction of the Dispersed Floccs into a Vehicle

It is difficult to disperse the chain floccs into polyurethane resin, presumably because of the "snowflake" structure of the floccs. Specifically the difficulty seems to be to obtain complete wetting of the floccs and remove air bubbles.

Preliminary studies showed that a resin and pigment mixed in a weight ratio that should have yielded a PVC of 35% typically led to a PVC the order of 10%. The use of vacuum treatment in attempting to remove bubbles, resulted in about a factor of two lower PVC than calculated.

Part of the problem is these pigments are fluffy. The pigment produced in our studies has a PVC of the order of 10-20% until a substantial pressure is applied to compress and break up the floccs.

This problem was solved by presizing the pigment before it was incorporated into a vehicle. This was accomplished by dispersing the pigment into methylethyl ketone and then dispersing in an ultrasonic bath for 0.5 - 1 hr. The slurry was then subjected to a mild ball

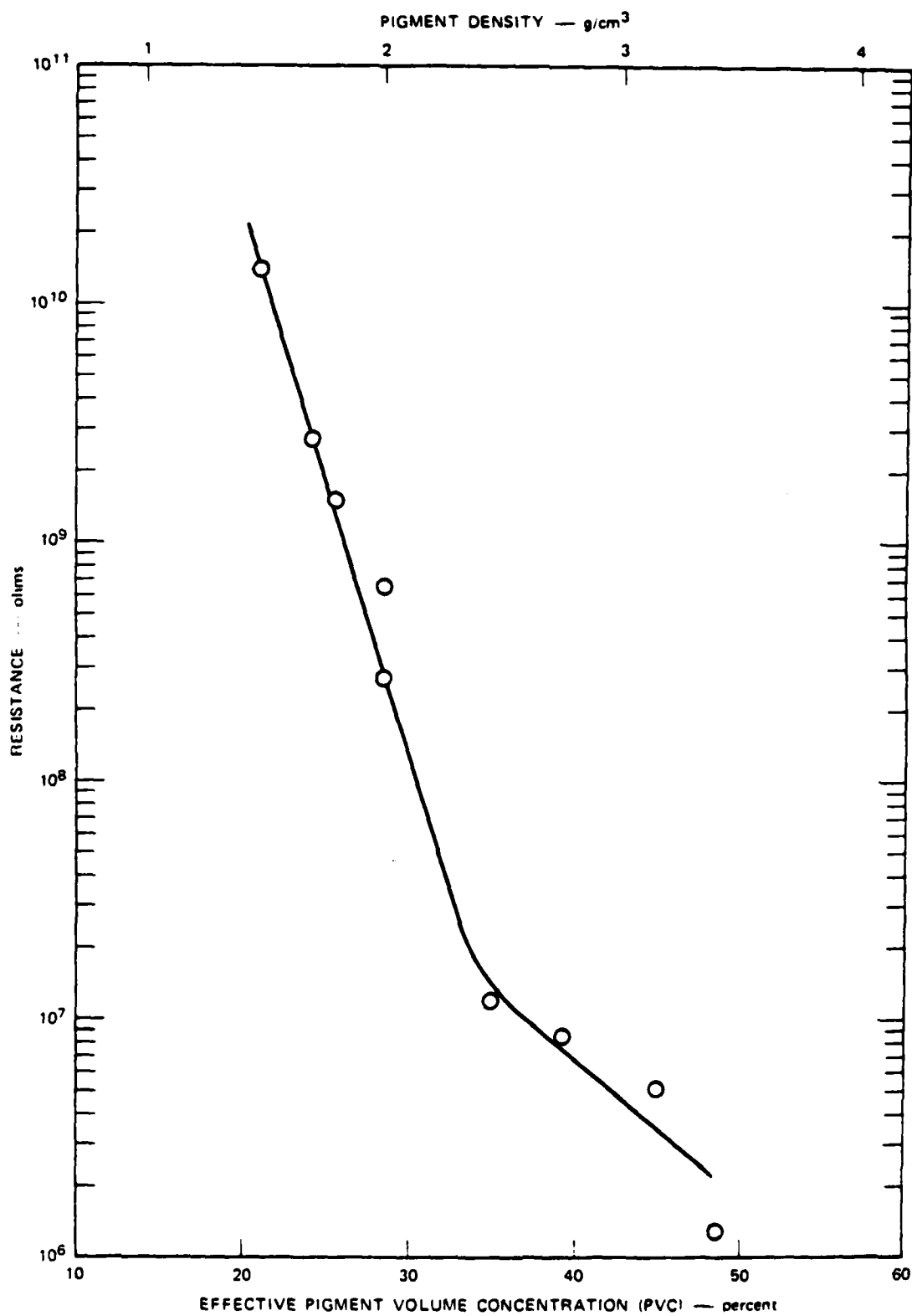
milling to break up the larger chain agglomerates that had been held together by strong crosslinks. Approximately 10% of the chains are destroyed in this process. If chains were of more uniform strength, the process could be modified to prevent any deterioration of the pigment. This treatment allowed incorporation of the pigment at higher PVC loadings.

E. Resistance of Chain Flocculated Pigments

1. Resistance Versus PVC in Air

We have made measurements of resistance versus PVC with no vehicle present. The measurement is simple--the pigment is simply crushed, and the resistance versus density (equivalent to PVC) is measured. The sample is inserted into a tube with a piston at each end to provide electrical control and to apply the pressure to crush the pigment. The resistance is then plotted as a function of the volume of the sample as the pigment was crushed in a press. For such a simple technique the results were quite reproducible. Figure 3 shows the results on an early sample consisting of SnO_2 and a SiCl_4 coupling agent, calcined at 1000° in air to convert all the SiCl_4 to SiO_2 . It is observed that beyond about 33% PVC the resistance tends to remain stable. In some measurements the PVC independent region began as low as 20% PVC. This feature encouraged us to conclude that for samples of low "bulk" resistance (low resistance at PVC = 100%) the use of chain flocs would permit satisfactory conductance with a 33% PVC or lower. This represents a substantial improvement in erosion resistance over untreated pigments, which require PVCs of 43-45% for conductance.

The new measurement technique described in the preceding paragraph was valuable for screening various treatments designed to improve the conductance of SnO_2 . Using this measurement, we were able



SA-6492-5

FIGURE 3 RESISTANCE OF CHAIN-FLOCCULATED SnO₂ AS A FUNCTION OF PVC

in the preliminary stages to bypass the more time-consuming procedure of paint formulation.

Most of our studies of interfloc resistance were made using an SnO_2 :Sb pigment prepared as described in Section IIA. As was described in Section C, subsection 2, the pigment has to be heated at 500°C after flocs had been grown to drive the reaction to completion and obtain a pigment of satisfactory strength. However after this treatment the resistance was found to be very high, too high to measure on a low PVC sample, the order of 10^8 ohm cm for a pressed pellet. The conductance versus temperature of the pressed pellet showed an unexpected high activation energy, the reason for which was not determined. A high temperature ($> 1000^\circ\text{C}$) calcination treatment on the pigment before pelletizing lowers the room temperature resistance to about 10^6 ohm cm. This is a significant improvement, but insufficient for a conducting paint. Such a calcination also improves the strength of the chains, and the activation energy for the resistance becomes low.

This is the expected behavior for SnO_2 particles separated by a thin layer of SiO_2 , and several methods were studied to reduce the residual resistance associated with this thin SiO_2 insulating layer. Two approaches were initially considered: (1) to lower the SiO_2 thickness, and (2) using SnCl_4 instead of SiCl_4 as the coupling agent to cement the particles. The use of SnCl_4 results in pure SnO_2 instead of SiO_2 -coated SnO_2 , so the conductance should automatically be satisfactory.

Because we had already developed the technique for adding SiCl_4 to the pigment, we initially tested the first approach. We tested various ways of removing controlled amounts of SiO_2 from the surface, with gas phase HF. An apparently satisfactory treatment was found exposing the pigment to about 40 torr HF for 45 ± 15 minutes at 500°C in a tube furnace. Tests showed that, at this pressure and time, more

than 1 hour HF exposure resulted in the disintegration of the chains; less than 30 min resulted in a high resistance pigment.

Measurements of the conductance versus PVC in air indicate that the flocs at 20% PVC yielded a satisfactory conductance.

Preliminary tests were made on this pigment incorporated into a vehicle. Epoxy resin was used in these tests for the vehicle so that shrinkage problems could be bypassed. However a serious problem that led to the discontinuation of this method was observed: when sufficient SiO_2 is removed to restore conductance to the chain flocs, so much is removed that the flocs are seriously weakened. Thus when they are incorporated into the vehicle, with the mechanical smearing and scraping attending this operation on a small sample, the flocs apparently disintegrate and the resistance is high.

The other method for eliminating the insulating SiO_2 layers is to use SnCl_4 as the coupling agent. Difficulties were identified in its use which were difficult to overcome. The reaction



apparently occurs efficiently only at high temperature (above about 350°C). At room temperature, a viscous deposit is formed that cannot support the chain structure. Thus, the chains cannot be satisfactorily cemented at low temperature, and when the field is turned off, the chains collapse. On the other hand the chains cannot be heated at high temperature before the application of the coupling agent. Without a coupling agent they disintegrate, presumably because at high temperature the dielectric constant of the particles decreases so that the dielectrophoretic force is insufficient to maintain their integrity.

The approach that successfully solved this difficulty was to deposit a SnO_2 layer on top of the SiO_2 layer used to cement the chain together. Using this general approach, two techniques have been developed which lead to highly conducting chains. The first technique consists of post-treating previously grown $\text{SnO}_2:\text{SiO}_2$ composite chains. In this method, the chains were placed in a tube furnace with provisions for continuously tumbling the pigment to aid in depositing a uniform coating. The pigment was heated in nitrogen to 400°C and a 6/1 ratio of $\text{H}_2\text{O}/\text{SnCl}_4$ vapours was continuously passed through the tube for periods of 1 to 2 hours. The second technique developed was to deposit a Cl-doped SnO_2 layer in situ as the final step in the chain growth process. The main feature of this technique is that the chains are heated to 400°C and the Cl-doped SnO_2 is deposited in the tube furnace, while the high voltage field is maintained. The advantage of maintaining the field is that the structure of the chain is retained, avoiding any deleterious cross linking during the deposition.

Chains prepared by the first technique were incorporated into a Viton vehicle at a loading of 33% PVC. These samples had a bulk resistivity of $3 \times 10^6 \Omega\text{-cm}$. Chains prepared by the second technique were incorporated into both Viton and polyurethane (Astrocoat) vehicles at 33% PVC. These samples has a resistivity the order of $50 \Omega\text{-cm}$. It should be noted that for a surface resistivity of $10^6 \Omega/\text{sq}$ a bulk resistivity of the order of $1000 \Omega\text{-cm}$ would be satisfactory.

2. Preparation and Testing of Optimized Coating

To improve the color of the coatings, emphasis in the last quarter has been placed on TiO_2 based chain flocs. A commercial white TiO_2 pigment from Dupont (R-906) was selected. Highly conducting chain flocs were produced using this pigment base and the chain growth procedure described in the preceding subsection.

Chains prepared with TiO_2 were incorporated into both fluoro-carbon (Viton) and polyurethane (Astrocoat) vehicles. Both these samples had a nominal resistivity of $250 \Omega\text{-cm}$. Measurements both through the coating and along the coating are in reasonable agreement. The conductivity of chains of this composition were also measured in air. At a PVC of 33% the resistivity was approximately $80 \Omega\text{-cm}$. All coating samples were grey to off-white in color. This coloration has been reported in the literature to be due to both SnO_2 impurities and excessive Cl doping inherent to the deposition technique.

The optical absorption of the pigment can be somewhat improved by heat treatment of the pigment in the $600\text{--}700^\circ\text{C}$ range. The heat treated material is light green. The heat treated material has a resistivity of approximately $1000 \Omega\text{-cm}$ as measured in air at a PVC of 33%. Heating the material in air at 1100°C for 1 hr yielded a white insulating material. This is assumed to be due to the simultaneous removal of Cl donors along with the annealing out of lattice strain. The 700°C heat treated material measured in polyurethane at a PVC of 22% had a resistivity of $4600 \Omega\text{-cm}$. Measurements of resistivity versus PVC were made because of the importance in erosion resistance.

Both heat treated and untreated pigments had less than an order of magnitude variation in resistivity versus PVC in the 25% to 40% PVC region, as measured in air. Unheat treated material cast in polyurethane had the same resistivity ($500 \Omega\text{-cm}$) at both 25% and 40% PVC within experimental error. This suggests that the possibility of yielding a highly erosion-resistant materials.

Material which had been diluted with 30% by weight pigment grade, unflocculated TiO_2 was also tested. At a total PVC of 33% the resistivity was nominally $3 \text{ K } \Omega\text{-cm}$. This coating was slightly off white. A sample of this coating on aluminum plate along with 1 gm of

untreated pigment has been submitted to WPAFB for testing as described in the next section.

F. Samples Submitted to WPAFB

In accordance with telephone discussions with Dr. W. Lehn, a sample of paint prepared with a polyurethane binder at 33% PVC has been submitted to the Coatings and Thermal Protection Materials Branch, Air Force Materials Laboratory. The coating formulation was prepared with a polyurethane binder, Astrocoat 8004,¹ at 33% PVC. The binder Astrocoat 8004 was mixed with Astrocoat 8101¹ catalyst at a ratio of 10 parts of 8004 to 1 part catalyst by simple hand stirring with a spatula. The pigment, a 50 percent by weight mix of stannic oxide with titanium dioxide, had a specific volume of 0.19 cc per gram. The pigment was weighed into the binder solution so as to give a 1:2 ratio by volume of pigment to coating solids. The pigment was mixed in vigorously with a spatula by hand. The mixture was then poured onto a 4-3/4" by 6" sheet of 20 mil anodized aluminum and drawn down with a doctor blade set at a 15 ml opening. The coating was allowed to dry at room temperature for two hours and was then cured in a convection oven set at 110°C for thirty minutes. Additionally a 1 g sample of chain flocculated pigment has been submitted. Unfortunately these were not available in time to include results of Air Force tests in this report.

III RECOMMENDATIONS

Further studies of the absorption mechanisms are needed for improvement of the pigment whiteness. Preliminary results have indicated that by proper heat treatment of the pigment one is able to get rid of most of the untreated color. The effects that should be studied are: The oxidation of SnO impurities, annealing of lattice strain, and the motion of donor impurities. A study of Cl incorporation and other donors and size compensating impurities may also prove useful in color control. A technique must be developed for annealing the SnO₂ layer until it is colorless without removal of the donors necessary for high conductivity.

Long term aging tests of the conductive coatings should be performed. Oxygen adsorption, impurity migration and vehicle-pigment interaction all may seriously affect the lifetime of the conductive coating. Along these lines, the effect of continuous mechanical deformation of these coatings should be investigated since it pertains directly to the problem of maintaining good interfloc contact over extended period of use.

Further uses of these pigments should be investigated in light of their unusual properties in selective optical absorption. Absorption in the visible, infrared, and microwave regions of the spectrum can be controlled almost independent of one another. Specifically, infrared absorption depends on the conductivity, microwave absorption depends on the conductivity and the length of the fiber, and visible light absorption depends on color center incorporation. The only directly coupled property is that for the coating to absorb in the microwave

region it must have a good conductance so it will absorb in the infra-red region. Thus a coating of unique hiding power is possible by using chain flocculated pigment.

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